



TITLE:

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CITATION:

Kawamoto, Haruo ...[et al]. Influence of neutral inorganic chlorides on primary and secondary char formation from cellulose. Journal of Wood Science 2008, 54(3): 242-246

ISSUE DATE:

2008-06

URL:

<http://hdl.handle.net/2433/240658>

RIGHT:

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Title Page

Original Article

**Title: Influence of neutral inorganic chlorides on primary and
 secondary char formation from cellulose**

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Keywords: cellulose, carbonization, primary char, secondary char, alkali metal chloride,
alkaline earth metal chloride

Abstract: Influence of various alkali and alkaline earth metal chlorides (LiCl, NaCl, KCl, MgCl₂ and CaCl₂) on primary and secondary char formation from cellulose was studied at 400°C. Secondary char was formed through secondary carbonization of the volatile products. All chlorides increased the primary char yield with decreasing the secondary char formation, and this situation was promoted in the order of alkaline earth Mg, Ca, alkali Li > alkali Na, K. Levoglucosan yield also decreased along with the secondary char yield. These results indicate that the reduced formation of volatile levoglucosan had relation to the decreasing yield of secondary char. Model experiment at 250 °C revealed that these chlorides, especially the two alkaline earth metals, had the catalytic action on the polymerization of levoglucosan. This catalytic polymerization would reduce the formation of volatile levoglucosan.

Introduction

Wood pyrolysis is the fundamental principle of various thermochemical processes of woody biomass such as carbonization, gasification and fast pyrolysis. The knowledge of the pyrolysis mechanism on a molecular basis is thus helpful to improve these conversion processes, i.e., increasing the product selectivity, alleviating the tar trouble in gasification and so on. This article focuses on the inorganic matter, that affects the pyrolysis reactions of cellulose greatly.

Influence of the inorganic matter on cellulose pyrolysis has been studied extensively, for understanding the behavior of woody biomass in thermochemical conversion processes.¹⁻¹⁸ Demineralization by acid washing the samples prior to pyrolysis usually increases the levoglucosan (1,6-anhydro- β -D-glucopyranoside) yield and reduces the char formation.^{1-3, 5} Influence of individual inorganic substance on cellulose pyrolysis has also been studied with ion-exchanged⁶⁻⁸ and impregnated^{2, 9-13} samples. According to the findings, the acidic substances enhance the formation of the dehydration products such as levoglucosenone and furfural, while some fragmented products including glycolaldehyde and hydroxyacetone are formed more preferentially with the basic substances.¹⁵⁻¹⁸ Some of these aspects are explained on the basis of their acidity and basicity. However, action of the neutral salts on cellulose pyrolysis is still unknown on a molecular basis.

As for neutral salts, many studies employed alkali metal halides.^{2, 9-11, 14} These halides are found to lower the degradation temperature slightly^{2, 11} and enhance the formation of char, CO, CO₂ and H₂O^{13, 14} with reducing the yield of levoglucosan.^{9, 13} Shafizadeh and Sekiguchi¹² reported by analyzing mellitic acid that NaCl-addition enhanced the formation of aromatic structures. There are, however, very few papers

which describe the influence of alkaline earth metal halides.^{4, 11}

Attention should be paid to the situation that a considerable amount of carbonized products (defined as “secondary char” in this article) was formed from the secondary carbonization of the volatile products after condensing near the outlet of the reactor with relatively low temperature. Practically, this type of char formation would be related to the clogging of the pyrolysis reactor. In our previous papers,^{19, 20} ring-opening polymerization of levoglucosan has been proposed as a key reaction to the carbonization. This secondary carbonization is also expected to be influenced by inorganic matter through changing the product compositions. However, the influence on the secondary carbonization has not been reported yet.

In this article, the action of alkali and alkaline earth metal chlorides on primary and secondary char formation is described by focusing on levoglucosan as a key intermediate to the secondary char formation.

Experimental

Materials

Filter paper (Kiriya Glass Co., oven dried at 105°C for 24 h) was used as a cellulose sample. Aqueous LiCl, NaCl, KCl, MgCl₂ or CaCl₂ solution (0.10, 0.050 or 0.010 mmol in 150 μ l) was added dropwise to the filter paper (37 mg). This amount of solution was completely absorbed by the filter paper. The resulting filter paper was dried in an oven at 105°C for 24 h before pyrolysis. The amount of the impregnation was 0.44, 0.22 and 0.044 mol/mol of the glucose-unit of cellulose. Control sample was also prepared with pure water (150 μ l) by the similar way.

Pyrolysis and product characterization

Pyrolysis was conducted with the apparatus reported in the previous paper.¹⁹ Sample was placed at the bottom of a round-shaped flask (30 ml volume) and the flask was attached with a cooling tube (120 mm long and 14 mm in diameter) and a nitrogen bag through a three-way tap. After replacing the air in the system with nitrogen, the flask was soaked in a salt bath ($\text{KNO}_3 / \text{NaNO}_3$, 1 : 1, w/w) (400 °C) for 10 min. The flask was immediately cooled with flowing air (30 s) and subsequently in cold water (3 min), and the carbonized paper (defined as “primary char” in this paper, Fig. 1) was taken out of the flask and weighed. The amount of the primary char was calculated by subtracting the weight of the chloride in the original paper from the weight of the carbonized paper, on the assumption that all the chloride could be included in the carbonized paper. The flask and the cooling tube were extracted with MeOH (5.0 ml) to give a MeOH-soluble fraction. The carbonized substance, which was observed near the top of the flask, is defined as “secondary char” in this paper (Fig. 1). The secondary char which was sticking on the wall of the flask was washed with water (5.0 ml) and dried before weighing. The amounts of the MeOH-soluble products and secondary char were calculated from the weight-difference of the glass ware before and after extraction. The MeOH-soluble fractions were analyzed by GPC with a Shimadzu LC-10A (column: Asahipak GS-220 HQ, eluent: water, flow rate: 1.0 ml/min, detector: RID, temperature: 40°C).

Influence on levoglucosan polymerization

Levogluconan (8.1 mg, 0.050 mmol) was taken into a round-shaped flask (30 ml) and dissolved in a chloride aqueous solution (0.0050 mmol in 0.10 ml). The resulting solution was evaporated *in vacuo* to form a thin film at the bottom of the flask. Heat treatment was conducted in N₂ with the similar apparatus as described in the pyrolysis section. To avoid the formation of the carbonization products, which make the investigation of the polymerization reactivity difficult, 250°C was chosen as a heating temperature. After 1 min heating at 250°C, reaction was quenched by cooling with flowing air (30 s) and in cold water (3 min). The reaction mixture was extracted with water (0.5 ml) and analyzed with GPC under the chromatographic conditions described above.

Results and discussion

Figure 2 summarizes the primary and secondary char yields at various chloride-addition-levels. Dotted line shows the total char yield [23%, primary (7%) + secondary (16%)] in pure cellulose (neat). With addition of chloride, the primary char yield increased up to 16 - 54% (excluding the amount of chloride) with decreasing the secondary char yield (0 - 16%). This situation was promoted with the increasing addition-level.

Alkaline earth metals (MgCl₂, CaCl₂) exhibited much greater influences than alkali metals (NaCl, KCl) except for LiCl. The influence of LiCl was rather similar to those of the alkaline earth metals. Mg (0.22, 0.44 mol), Ca (0.22, 0.44 mol) and Li (0.44 mol) reduced the secondary char yields up to undetectable levels, while the primary char yields increased about 3.6 – 7.3 times as compared with pure cellulose. Consequently, their total char yields substantially increased (1.5 – 2.3 times). Contrary to this, the

total char yields from the NaCl- and KCl-impregnated samples were not affected greatly (1.2 – 1.5 times).

Gel permeation chromatograms of the MeOH-soluble fractions at 0.44 mol/mol of the glucose-unit are shown in Fig. 3. The peak area in the chromatogram decreased in the order of neat > Na, K > Li, Mg, Ca, and this order was quite similar to that observed in the secondary char formation. The peak areas at 10 min, which correspond to the yield of levoglucosan, were reduced by Na-, K- and Ca-impregnation, and levoglucosan was not detected from the Li- and Mg-impregnated samples. Figure 4 summarizes the primary, secondary and total char yields as plotted against the levoglucosan yields. Some positive correlation existed between the secondary char and levoglucosan yields, while the primary char yield was negatively correlated with the levoglucosan yield. Due to these opposite relationships between primary and secondary char yields, the total char yields from the neat and Na- and K-impregnated samples were almost independent of the levoglucosan yield.

Influence of the chlorides on the polymerization of levoglucosan is discussed from the GPC chromatograms measured for the heat treated mixtures of levoglucosan and chlorides (1:0.1, mol/mol, N₂ / 250°C / 1 min) in Fig. 5. Intensity of the peak area observed in the higher MW region than levoglucosan increased with addition of chloride. Polymerization reactivity was evaluated by introducing the “polymerization index”, which is defined as equation (1).

$$\text{Peak area (higher MW region than levoglucosan)} / \text{peak area (levoglucosan)} \quad (1)$$

The larger the polymerization index becomes, the greater is the catalytic activity. The obtained polymerization indexes are summarized in Fig. 6. All these chlorides had the

catalytic action on the polymerization of levoglucosan. The alkaline earth metals, which substantially increased the primary and total char yields had especially high catalytic activities. The catalytic activity of LiCl was weak like other alkali metals, although the enhancing effect on the primary char formation was much greater than NaCl and KCl.

Based on these lines of evidence, the influence of alkali and alkaline earth metal chlorides on primary and secondary char formation from cellulose is discussed in terms of the formation of volatile levoglucosan. In pure cellulose, substantial amount of levoglucosan vaporizes and condenses at the reactor-wall with lower temperature, where levoglucosan is subject to secondary carbonization (Fig. 7). Consequently, secondary char yield depends on the amount of volatile levoglucosan. Kawamoto et al.^{19, 20} have reported that the ring-opening polymerization of levoglucosan is a key reaction for the carbonization. Reduction of the amount of volatile levoglucosan induced by alkali and alkaline earth metal chlorides would be related to the inhibition of the secondary char formation.

The catalytic action of these chlorides on the polymerization of levoglucosan would reduce the amount of volatile levoglucosan, although they would have complex action on cellulose pyrolysis. In the following paper,²¹ the action of MgCl₂ and CaCl₂ as Lewis acids to promote the solid-state hydrolysis have been found at elevated temperature. Affinity of Mg²⁺ or Ca²⁺ to the ring-oxygen of levoglucosan has been used to explain the catalytic activity. Relatively strong influence of LiCl on cellulose carbonization, which has low catalytic activity, suggests that other mechanisms also play important roles, although further study is necessary to clarify the mechanism.

Conclusions

Alkali and alkaline earth metal chlorides increased the primary char yield with inhibiting the secondary char formation. The yield of levoglucosan, the important intermediate in cellulose pyrolysis, also substantially reduced with these salts. Especially strong actions were observed for the alkaline earth metal chlorides, and these chlorides had the strong catalytic activities on the polymerization of levoglucosan. Based on these results, inhibition of the secondary char formation would be related to the reduced formation of volatile levoglucosan in the presence of these salts.

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*1: peak area (higher MW products than levoglucosan) / peak area (levoglucosan) in GPC.

Figure 7. Levoglucosan as a key intermediate for the secondary char formation in cellulose pyrolysis.

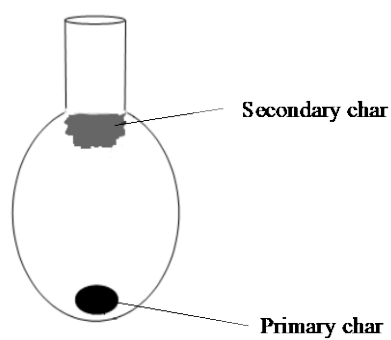


Figure 1. Primary and secondary char formation.

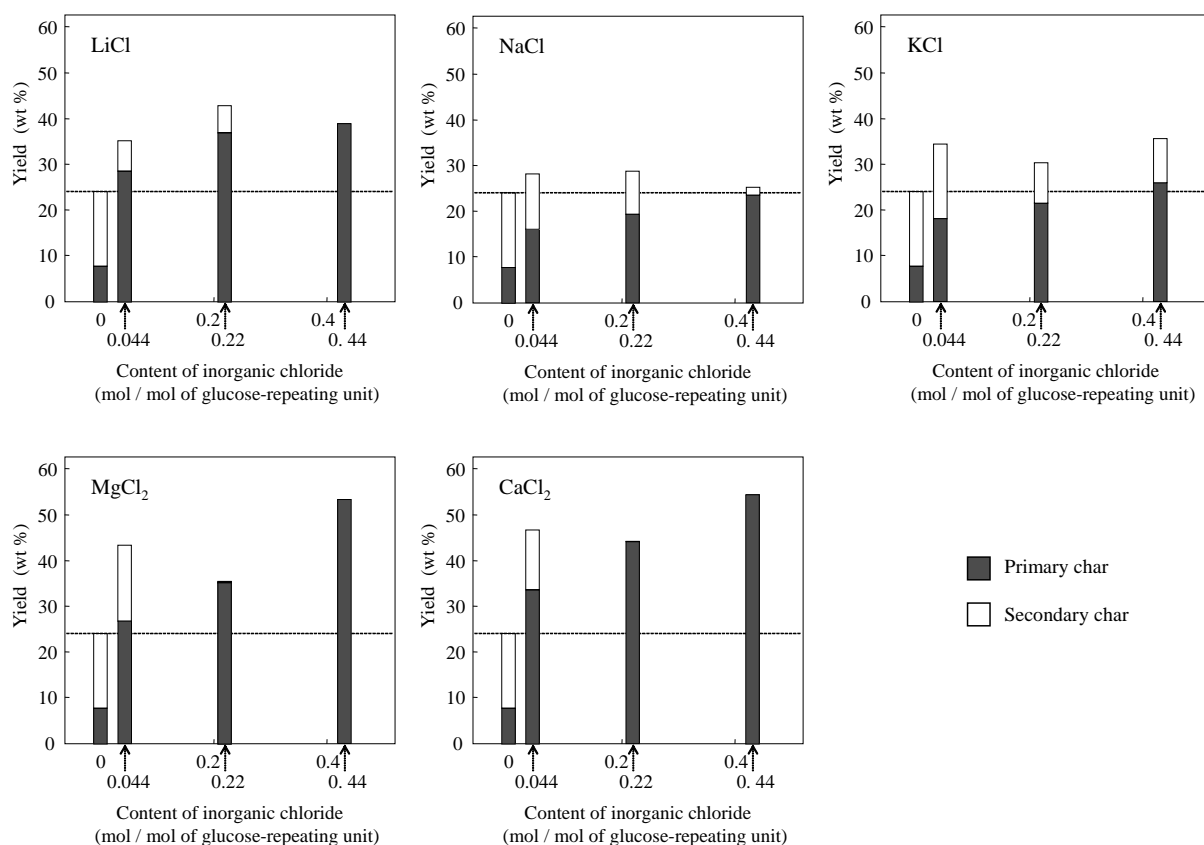


Figure 2. Influence of the inorganic chlorides on primary and secondary char formation from cellulose (N_2 / $400^\circ C$ / 10 min).

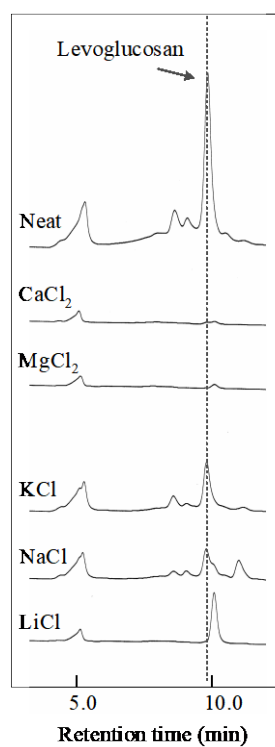


Figure 3. Gel permeation chromatograms of the MeOH-soluble fractions obtained from the chloride-impregnated cellulose samples (N_2 / 400°C / 10 min).

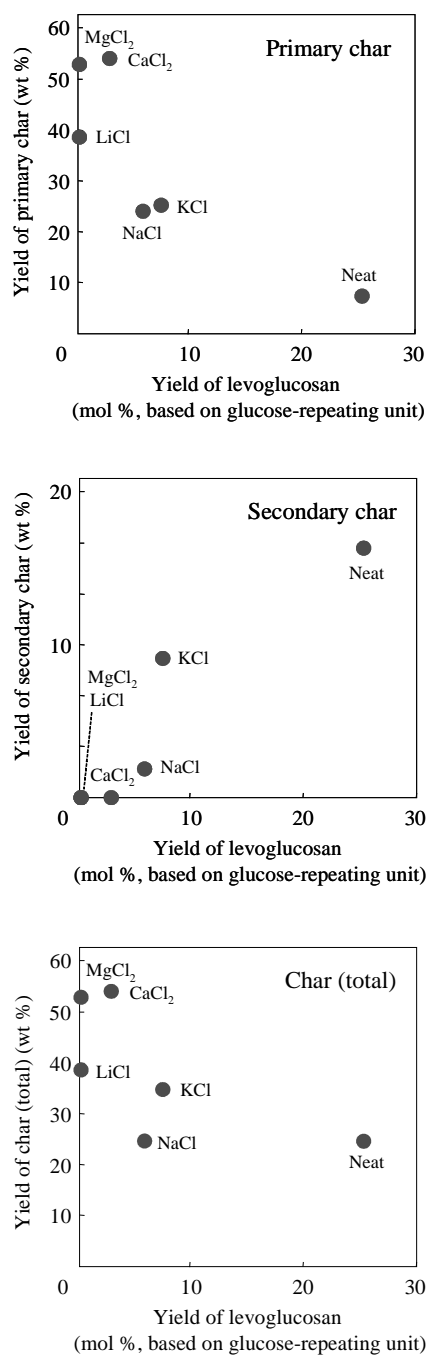


Figure 4. Relationships between the primary, secondary and total char yields with the levoglucosan yield.

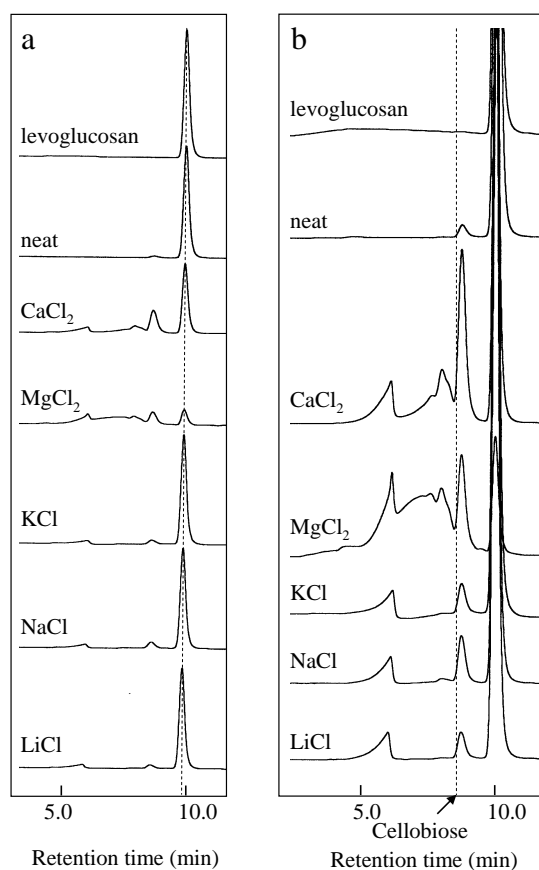


Figure 5. Gel permeation chromatograms of the heat treated mixtures of levoglucosan and chlorides (levoglucosan : chloride = 1 : 0.1, mol/mol, N_2 / 250°C / 1 min).

b: enlarged chromatograms.

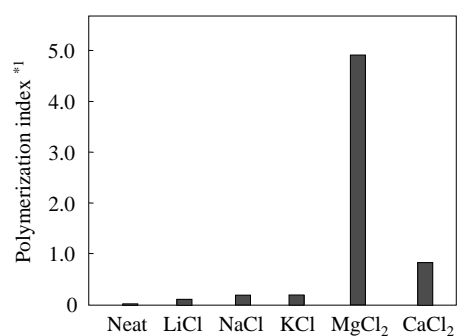


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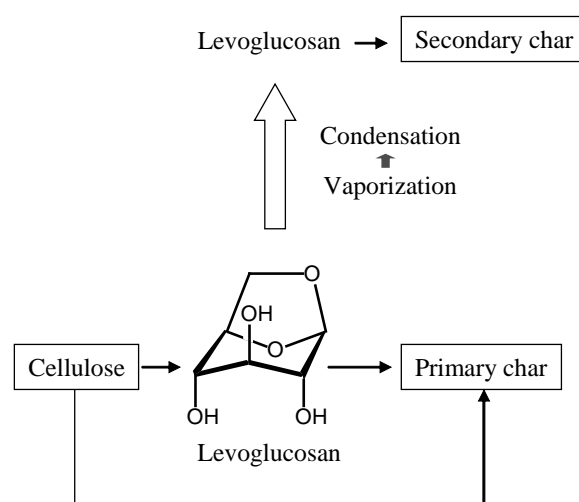


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